Physical Properties, Characterization & Interaction Mechanism Study Between Iron (II) Sulphate ($FeSO_4$) and Glutamic Acid, N,N-Diacetic Acid, Tetrasodium (GLDA)

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ABSTRACT

Scale formation often occurs causing an expensive production problems and usually lowering the oil production rates. Sulphate minerals are amongst the most common scale components in oilfield production wells and surface facilities. Mechanical techniques or chemical treatments are traditionally used to cut through the scale blockage. Water jets are example of mechanicals technique meanwhile HCl and EDTA usually use for the chemical techniques. Thus, the current study was conducted to investigate the solubilities one of the sulphate mineral namely Iron (II) sulphate ($FeSO_4$) when react with solvent of Glutamic acid, N,N-diacetic acid, tetrasodium or also known as GLDA. It has a pH of 4.11 and is heavier than water as its density is 1.2710 g/cm^3 and can be used as alternative to nitrilotriacetic acid (NTA) and ethylene diamine tetraacetic acid (EDTA). It has an exceptional high solubility over a wide pH range and is based on a natural and sustainable source which it is contain 86% of renewable raw and non-fossil materials. In this study, it was found that $FeSO_4$ scale is completely soluble when mix with the GLDA solvent. From the observation, mass ratio of GLDA: $FeSO_4$ is 5:2. Based on FTIR and NMR spectrum, it showed that physical interaction occurred between GLDA and $FeSO_4$. Results obtained from the experiment show that is suitable for removing a scaling basically on its physical properties and characterization.

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ABSTRAK

Pembentukan kerak sering berlaku menyebabkan masalah pengeluaran yang mahal dan biasanya mengurangkan kadar pengeluaran minyak. Mineral sulfat adalah antara komponen kerak yang paling biasa dalam telaga pengeluaran minyak dan kemudahan permukaan. Teknik mekanikal atau rawatan kimia biasanya digunakan untuk mengurangkan kerak yang tersumbat. Jet air adalah contoh teknik mekanikal manakala HCl dan EDTA biasanya digunakan untuk teknik kimia. Oleh itu, kajian semasa telah dijalankan untuk menyiasat kebolehlarutan salah satu mineral sulfat iaitu ferum (II) sulfat ($FeSO_4$) apabila bertindak balas dengan pelarut asid glutamik, N, asid N-diacetic, tetrasodium atau juga dikenali sebagai GLDA. Ia mempunyai pH 4.11 dan lebih berat daripada air kerana ketumpatannya adalah 1,2710 g / cm^3 dan boleh digunakan sebagai bahan alternatif kepada asid nitrilotriacetic (NTA) dan ethylene asid diamine tetraacetic (EDTA). Ia mempunyai kebolehlarutan yang sangat tinggi dalam julat pH yang luas dan adalah berdasarkan kepada sumber semula jadi dan lestari yang ia mengandungi 86% daripada bahan-bahan mentah fosil dan tidak boleh diperbaharui. Dalam kajian ini, didapati bahawa kerak $FeSO_4$ benar-benar larut apabila di campuran dengan pelarut GLDA . Dari pengiraan, kita boleh mendapatkan nisbah jisim GLDA: $FeSO_4$ adalah 5:2. Berdasarkan spektrum FTIR dan NMR, ia menunjukkan bahawa interaksi fizikal berlaku antara GLDA dan $FeSO_4$. Keputusan yang diperolehi dari eksperimen ini menunjukkan ia sesuai untuk membuang kerak berdasarkan kepada sifat-sifat fizikal dan penciriannya.

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LIST OF ABBREVIATIONS

Ag	Silver
APCAs	Aminopolycarboxylic Acids
$BaSO_4$	Barium Sulphate
$CaSO_4$	Calcium Sulfate
CHNSO	Macro Elemental Analyzer CHNSO
Cu	Copper
DETPMP	Diethylenetriaminepenta (methylenephosphonic Acid)
DS	Polyaspartic acid
DTPA	Diethylenetriaminepentaacetic acid
EDDS	Ethylenediamine-N, N Œ-disuccinic acid)
EDTA	Ethylenedinitrilotetraacetic Acid
Fe	Iron
FeS	Iron(II) sulfide or ferrous sulfide
$FeSO_4$	Iron (II) Sulphate
FT-NMR	Fourier Transform Nuclear Magnetic Resonance
FTIR	Fourier transforms infrared spectroscopy
GLDA	Glutamic acid, N,N-diacetic acid, tetrasodium
HCl	Hydrochloric Acid
HEDTA	Hydroxyethylethylenediaminetriacetic acid
ICP-MS	Inductive Coupled Plasma - Mass Spectrometer
IDS	Iminodisuccinic acid
MGDA	Methylenglycine diacetic acid
Mn	Manganese
NTA	Nitrilotriacetic acid
PbS	Polybutylene succinate
PPCA	Polyphosphonocarboxylic acid
ZnS	Zinc sulfide

1 INTRODUCTION

1.1 Motivation and statement of problem

Scale formation in surface and subsurface oil and gas production equipment has been recognized to be a major operational problem. It has been also recognized as a major cause of formation damage either in injection or producing wells. Scale contributes to equipment wear and corrosion and flow restriction, thus resulting in a decrease in oil and gas production. Experience in the oil industry has indicated that many oil wells have suffered flow restriction because of scale deposition within the oil producing formation matrix and the downhole equipment, generally in primary, secondary and tertiary oil recovery operation as well as scale deposits in the surface production equipment.

They may occur downhole or in surface facilities. It is an assemblage of deposits that cake perforation, casing, production tubing, valves, pumps and downhole completion equipment which causes clogging in the wellbore The consequence could be production-equipment failure, emergency shutdown, increased maintenance cost, causes prevention of fluid flow in the equipment and an overall decrease in production efficiency. The failure of production equipment and instruments could result in safety hazards (Yeboah et al., 1993).

Figure 1-1: Scaling inside the wellbore **(Crabtee et al., 1999).**

Scale that mostly found in oil fields forms from water that occur naturally in reservoir rocks, which as a result of production water becoming oversaturated with scaling components when two incompatible water meet down hole. Changes in temperature, pressure, pH, and CO_2/H_2S partial pressure could also contribute to scale formation (Mackay et al., 2003; Moghadasi et al., 2003a).

It begins to form when state of any natural fluid is perturbed such that the solubility limit for one or more components exceeds. Mineral solubilities depend on temperature and pressure. As temperature increase, water solubility of mineral increase which will cause more ions dissolved at higher temperature. Calcium carbonate scale deposition induces important damage in the domestic, agricultural or industrial installations using natural waters (pipe blocking, membrane clogging, efficiency decay of heaters or heat exchangers, etc.).(Alimia et al., 2009). The buildup of scale inside wellbores also can cause a millions of dollars in damage to the wellbores every year.

Calcium sulfate (anhydrite, gypsum), barium sulfate (barite), strontium sulfate (celestite) and calcium carbonate are the common type of scaling. Other less common scales have also been reported such as iron oxides, iron sulfides and iron carbonate. Mineral scale such as $CaCO_3$ can be dissolved with acids, while others cannot. Sometimes waxy coatings of hydrocarbons protect scale from chemical dissolvers. The accumulated solid layers of impermeable scale can line production tubing and cause it to block and are less easily removed. Moreover, common hard scales like Barium sulfate ($BaSO_4$) are extremely resistant to chemical and mechanical removal (Crabtee et al., 1999).

Many of the recent studies used artificial hard water to investigate calcium carbonate scaling primarily due to its easier preparation, faster time for scale formation, possibilities of higher calcium carbonate concentration and more controlled initial water chemistry. (Leonard et al., 2001). The successive pressure drops lead to release of the carbon dioxide with an increase in pH value of the produced water and precipitation of calcium carbonate (Mackay et al., 2003).

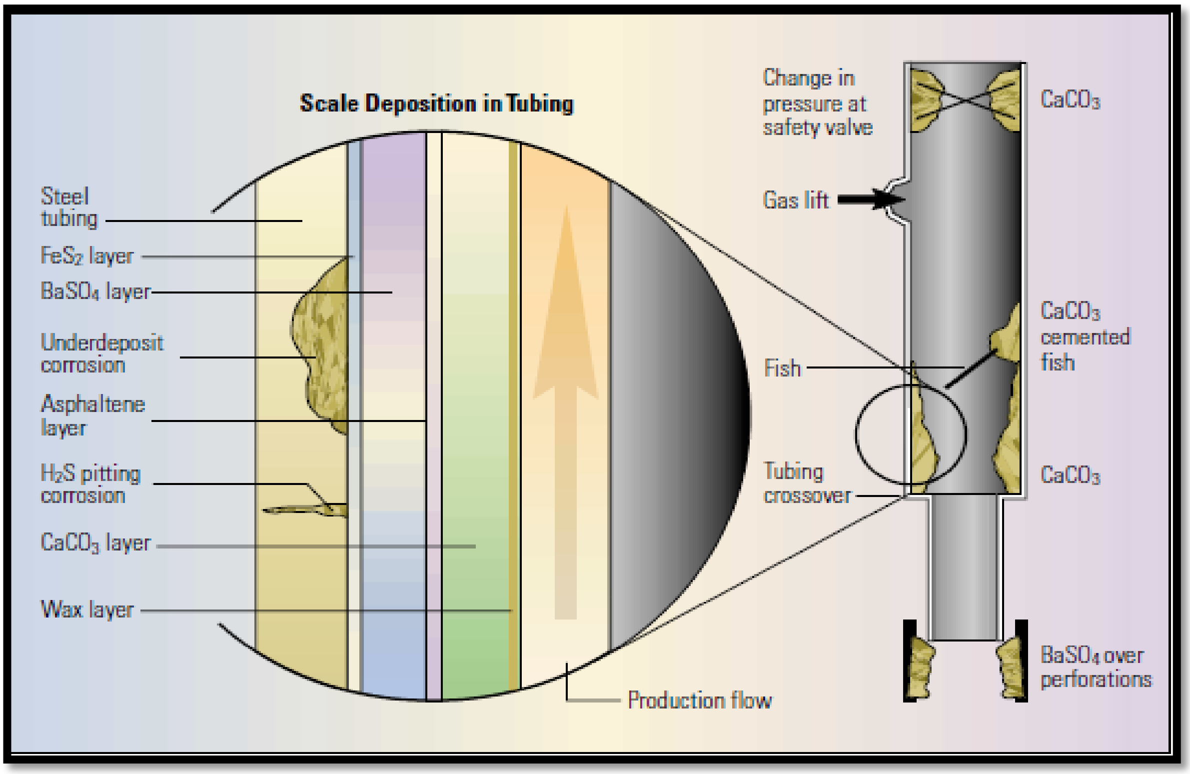

Figure 1-2 : Scaling inside tubing **(Crabtee et al., 1999).**

Figure 1-2 show the scale in tubing. The location of scale deposits in tubing can vary from downhole perforations to the surface where it constrains production through tubing restrictions, blocked nipples, fish, safety valves and gas-mandrels. Scale often layered and sometimes covered with waxy or asphaltene coating (insert). Pitting and corrosion on steel can develop under the scale due to bacteria and sour gas, diminishing steel integrity (Crabtee et al., 1999). The formation of scale will slow down the transporting of oil production in the reservoir.

The two main types of scale which are commonly found in the oilfield are carbonate and sulfate scales. These scales are sulfates such as calcium sulfate (anhydrite, gypsum), barium sulfate (barite), and strontium sulfate (celestite) and calcium carbonate. Other less common scales have also been reported such as iron oxides, iron sulfides and iron carbonate. The common types of scales are listed in Table 1-1, along with primary variables that affect their solubility:

Table 1-1: Most common oilfield scale **(Moghadasi et al., 2003a).**

Name	**Chemical Formula**	**Primary Variables**
Calcium Carbonate	$CaCO_3$	Partial pressure of CO_2, temperature, total dissolved salts, pH
Calcium Sulfate: Gypsum Hemihydrate Anhydrite	$CaSO_4.2H_2O$ $CaSO_4.1/2H_2O$ $CaSO_4$	Temperature, total dissolved salts, pressure
Barium Sulfate	$BaSO_4$	Temperature, pressure
Strontium Sulfate	$SrSO_4$	Temperature, pressure, total dissolved salts
Iron Compounds: Ferrous Carbonate Ferrous Sulfide Ferrous Hydroxide Ferrous Hydroxide	$FeCO_3$ FeS $Fe(OH)_2$ $Fe(OH)_3$	Corrosion, dissolved gases, pH

An oilfield menace can be smothering a productive well within 24 hours. Scale deposition can cause clogging in the wellbore and will preventing the fluid flow. The scale formation can block flow by clogging perforations or forming a thick lining in production tube. Besides, it also can coat and damage down hole completion equipment, such as safety valves and gas-lift mandrels (Crabtee et al., 1999).

The effects of scale can be dramatic and immediate as example in one North Sea well in the Miller field, engineers were shocked to see production fall from 4770 m^3/d to zero in just 24 hours (Brown, 1998). The cost can be enormous also. Curing scale problem costs the industry hundreds of millions of dollars per year in lost production. Until recently, ways to treat the problem were limited and sometimes ineffective.

1.2 Objectives

The aims of this work are to investigate the physical properties of GLDA, to analyse the characteristics based on CHNOS, ICPMS, FTIR and NMR as well as to analyse the dissolution of $FeSO_4$ in GLDA.

1.3 Scope of this research

The following are the scope of this research:

i. The correlation of results obtained from characterizations tests with the chemical formula of GLDA.
ii. Experimental analysis of the amount of $FeSO_4$ ranging from 0.5g to 5.5g of $FeSO_4$ dissolved in GLDA at room temperature and atmospheric pressure.
iii. The differences between the pure GLDA and GLDA with maximum amount of $FeSO_4$ salts in terms of its physical properties.

1.4 Organization of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 1 will includes the introduction of scale, type of scale, the common scale that can be found in reservoir and also the formation of scale. Scaling problem is also one of the serious problem that occur in reservoir, due to the problem, a lot of previous studies focusing on method to removing the scale. Objective and scope for the experiment will be provided in this chapter.

Chapter 2 provides a general description on the scale characteristics in the reservoir, as well as the formation of the scale. A brief review on the type of scale, solubilities effect in scaling formation and the current reagents use to remove the scale. This chapter also provides an introduction about the GLDA as the removing agents for scaling. This chapter will summary of the alternative removing agents to remove scaling.

Chapter 3 gives a review of how the experiment will be conduct. The manipulated and corresponding variables are choosing. The types of equipment, model, brand, function, method, precautions and others will be brief in this chapter. The method for analysis used also will be provided in this chapter.

Chapter 4 is will include the result of the previous studies on scaling involving EDTA, and HCl. In this chapter also will be provides with result of experiment on solubilities of $FeSO_4$ with GLDA. Solubilties of solution will be determining using experimental process. The physical properties and characterizations on GLDA will be discussed in this chapter. The experimental result for physical properties and characterizations on GLDA will be compared with theoretical result.

Chapter 5 draws together a summary of the thesis and outlines the conclusion of the experiment. Either the objective of the experiment is achieved or not. The future works for this experiment also will be brief in this chapter.

2 LITERATURE REVIEW

2.1 Overview

This paper presents the experimental studies for solubilities of $FeSO_4$ for reservoir stimulation. The current removing agent will be identify and explain. The explanations of GLDA as chosen removing agents for this experiment also will describe. Scale is an assemblage of deposits that cake perforation, casing, production tubing, valves, pumps and downhole completion equipment which causes clogging in the wellbore. Scale will cause prevention of fluid flow in the equipment.

Scale that mostly found in oil fields forms from water that occur naturally in reservoir rocks, which as a result of production water becoming oversaturated with scale components when two incompatible water meet down hole (Mackay et al., 2003; Moghadasi et al., 2003a). Scale begins to form when state of any natural fluid is perturbed such that the solubility limit for one or more components exceeds. Mineral solubilities depend on temperature and pressure of the mineral.

Scale can occur at/or downstream of any point in the production system, at which supersaturation is generated. Supersaturation can be generated in single water by changing the pressure and temperature conditions or by mixing two incompatible waters. Changes in temperature, pressure, pH, and CO_2/H_2S partial pressure could also contribute to scale formation (Mackay et al., 2003; Moghadasi et al., 2003a). If the temperature increases, the water solubility of mineral increase, as a result, this will cause more ions dissolved at higher temperature.

The most common mineral scales are sulfate and carbonate-based minerals. However, scale problems are not limited to these minerals and there have recently been reports of unusual scale types such as zinc and lead sulfides (Collins and Jordan, 2003).

Moreover, the formation of mineral scale associated with the production of hydrocarbons has always been a concern in oilfield operation. Depending on the nature of the scale and on the fluid composition, the deposition can occur inside the reservoir which causes formation damage (Khatib, 1994; Krueger, 1986; Lindlof and Stoffer, 1983; Moghadasi et al., 2003a) or in the production facilities where blockage can cause severe operational problems.

During petroleum exploration and production, when fluids are introduced into a porous rock, its original purpose is to increase the recovery of hydrocarbon. However, because the incompatibility between injected and native fluids, change of reservoir rock properties can often be expected. During various oil exploitation activities, the following sections describe the potential causes of formation damage (Moghadasi et al., 2002):

i. Drilling

   During drilling, higher pressure is required in the wellbore to control the formation being penetrated, the pressure differential will result in invasion of mud solids and mud filtrate into reservoir rock near wellbore. Solid invasion is strongly influenced by particle size and pore throat size distribution.

ii. Production

   During the oil and gas production the temperature and pressure in reservoirs are constantly altering. Organic scale such as asphaltenes and paraffin waxes may deposit outside of the crude oil to plug the formation. Inorganic salts such as calcium carbonate and barium sulfate may also precipitate out of the aqueous phase to block flow paths. The great pressure gradient near the wellbore often is capable of mobilizing fines residing on the surface of pore wall around the producing wells to cause fines migration.

iii. Water Flooding

   Combination of the injected water with the indigenous reservoir fluids is an important factor that influences the success of a water flooding program. The ions contained in the injected fluid may react with the ions in the native fluid to insoluble precipitates.

iv. Stimulation

   Most stimulation operations involve chemical treatments. Reactions of different kinds occur when chemicals are introduced into formations. Some of the reactions have adverse effects on formation permeability.

2.2 Type of scaling/cavity

Many histories of oil well scaling by calcium carbonate, calcium sulfate, strontium sulfate, and barium sulfate have been reported (Mitchell et al., 1980; Lindlof and Stoffer, 1983; Vetter et al., 1987). The chief source of oilfield scale is mixing of incompatible waters. Two waters are called incompatible if they interact chemically and precipitate minerals when mixed. A typical example of incompatible waters are sea water with high concentration of SO_4^{-2} and low concentrations of Ca^{+2}, Ba^{+2}/Sr^{+2}, and formation waters with very low concentrations of SO_4^{-2} but high concentrations of Ca^{+2}, Ba^{+2} and Sr^{+2}. Mixing of these waters, therefore, causes precipitation of $CaSO_4$, $BaSO_4$, and/or $SrSO_4$. Field produced water (disposal water) can also be incompatible with seawater.

Iron sulfide species have been known to cause operational problems in the oil industry. Iron sulfide scale is present in oil and gas producing wells, sour wells and water injectors where the injected water has high sulfate content. The sources of iron are the formation brines especially in sandstone formations and the well tubular. Iron produced by corrosion processes can be minimized by employing various corrosion protection techniques (Nasr-El-Din & Al-Humaidan, 2001).

According to (Raju et al., 2003) the disposal water contains dissolved H_2S, whereas the aquifer water contains dissolved iron. When these two waters are mixed together, H_2S reacts with the iron ions and precipitates iron sulfide species. The iron ions and H_2S will form a scaling of FeS. This reaction is commonly happen in the reservoir during the oilfield production. The reaction is shown in equation below:

$$Fe^{++} + H_2S \longleftrightarrow FeS + 2H^{+}$$

Several heavy metal sulfides (PbS, ZnS, FeS etc.) are found in scale deposits formed by the flow of high-enthalpy and high salinity geothermal brines, such as those in Salton Sea, California (Skinner et al., 1967), Andritsos Karabelas, and in Asal, Djibouti (Criaud & Fouillac, 1989). These scales are Iron sulfide scales are also encountered in several low temperature geothermal systems in the Dogger region (Criaud & Fouillac, 1989). In geothermal plants, as already reported, several sulfide phases precipitate at the pipe wall to form the sulfide-rich scales.

Consequently, the study of scaling phenomena due to simultaneous precipitation of several metal sulfides may be also of great interest. An experimental study of deposition of mixed sulfides (eg. PbS, ZnS, FeS), however, is hindered by the large differences in solubility (several orders of magnitude) of the various compounds at temperatures close to ambient, and by the fact that at these conditions, amorphous ZnS and FeS (Rickard, 1989) phases may be formed.

The study of iron sulfide scale formation is also of great importance since it is the most abundant component in sulfide-rich scales. Despite the fact that the iron-sulphur system is perhaps the most extensively studied binary sulfide system, the laboratory synthesis and the identification of the various phases have encountered considerable difficulties. The reaction between sulfide species and ferrous ions at atmospheric conditions and close to neutral pH leads to the precipitation of a black iron (II) sulfide (Morse et al., 1987) that slowly transforms. This initial product is seemingly an amorphous precipitate prone to oxidation.

2.3 Solubility of scale formation

Solubility is defined as the limiting amount of solute that can dissolve in a solvent under a given set of physical conditions. When a sufficiently large amount of solute is maintained in contact with a limited amount of solvent, dissolution occurs continuously till the solution reaches a state when the reverse process becomes equally important. This reverse process is the return of dissolved species (atoms, ions, or molecules) to the undissolved state, a process called precipitation (Mohammed A.B., 2008).

Dissolution and precipitation happen constantly and at the same rate, the measure of dissolved solute present in a given amount of solvent stays consistent with time. The methodology is one of dynamic equilibrium and the solution in equilibrium state is known as a saturated solution. The concentration of the saturated solution is referred to as the solubility of the solute in the given solvent. Accordingly, solubility of a solute is characterized as its maximum concentration which can exist in solution under a given set of states of temperature, pressure and concentration of other species in the solution. According to Lindlof and Stoffer (1983), strontium sulfate solubility is decreased by the common ion effect; the supersaturation becomes a disproportionately higher percentage of total strontium sulfates in the solution.

A solution that contains less solute than required for saturation is called an unsaturated solution. A solution, whose concentration is higher than that of a saturated solution due to any reason, such as change in other species concentration, temperature, etc., is said to be supersaturated. When the temperature or concentration of a solvent is increased, the solubility may increase, decrease, or remain constant depending on the nature of the system. For example, if the dissolution process is exothermic, the solubility decreases with increased temperature; if endothermic, the solubility increases with temperature (Mohammed A.B., 2008).

Both unsaturated and saturated solutions are stable and can be stored indefinitely whereas supersaturated solutions are generally unstable. However, in some cases, supersaturated solutions can be stored for a long time without exhibiting any change and the period for which a supersaturated solution can be stored depends on the degree of departure of such a solution from the saturated concentration and on the nature of the substances in the solution. There are two solubilities of scales:

i. Calcium, strontium, barium sulfates, and calcium carbonate solubilities
ii. Zinc sulfide, lead sulfide, and iron sulfide solubilities

Lead and zinc sulfide solubility is much lower even than iron sulfide, which is the common sulfide in oil field situations. The very low solubility of lead and zinc sulfide would make it doubtful that zinc/lead and sulfide ions could exist together in solution for any length of time. It is more probable that the zinc/lead ion source mixes with the hydrogen sulfide-rich source inside the close wellbore or the production tubing during fluid extraction; structure then on, changes in temperature, solution pH, and residence time control where scales deposit within the process system.

2.4 Current killing agent to remove scaling

Scale inhibitors that are periodically pumped down production wells and into the producing formation for short distances around the wellbore have been developed and are widely utilized. The inhibitor contacts the formation and is adsorbed onto the reservoir petrofabric. It is later slowly released into the produced fluids, thereby inhibiting the formation of sulfate scales for some period of time, usually several months. When the inhibitor concentration levels fall too low to be effective, the well is again squeezed with chemical and the cycle is repeated. This technique is widely known as squeeze inhibition (McElhiney et al., 2001).

In the majority of cases, a good scale inhibitor should be effective at 5-15 ppm in clean water. However, if substantial amount of suspended solids are present, higher inhibitor concentrations will be necessary. Moreover, the reason being that the inhibitor will adsorb onto surface of the solids in the water, thereby reducing the amount available to inhibit scale formation.

The formation of mineral scale (carbonate/sulfate/sulfide) within the near wellbore, production tubing and topside process equipment has presented a challenge to the oil and gas industry for more than 50 years. Chemical methods to control scale have been developed including scale squeeze treatments and continual chemical injection. A key factor in the success of such treatments is the understanding of chemical placement and the effectiveness of the treatments chemicals (Jordan et al., 2006b).

Squeezing is the most common method for scale control downhole. Scale inhibitor, diluted in brine, is displaced into the producing formation where it is retained and then released slowly back into the aqueous phase during normal well production. Squeeze inhibition is effective in a wide variety of situations; however, it has some drawbacks. The squeeze chemical, often a phosphonate or high molecular weight sulphonate, is usually dissolved and diluted in water for transport down the wellbore.

Several challenges must be overcome in order to develop an effective combined scale removal and scale inhibition treatment. The most notable are (Smith et al., 2000):

i. Cost

- The combined treatment has to offer an economic advantage when compared to serial stimulation and inhibition treatments.

ii. Corrosion control

- The scale inhibitor must not cause a significant change in the corrosivity of the stimulation system. If the stimulation system requires the use of a corrosion inhibitor then the scale inhibitor must not prevent its function.

iii. System compatibility

- The scale inhibitor must be completely compatible with the stimulation system, both live and spent. The combined treatment must also be compatible with formation fluids.

iv. Inhibitor adsorption

- The scale inhibitor has to effectively adsorb onto the formation, throughout the potential pH range of the stimulation system.

v. Process compatibility

- The flow-back after a combined scale removal and inhibition treatment must have no opposed effect on the process system operation.

Several combined scale removal and inhibition systems could be considered in order to meet these challenges. Hydrochloric acid (HCl) may be the most cost effective treatment to remove calcium carbonate, but corrosion control, system compatibility and inhibitor adsorption may all be difficult in a combined treatment. Conversely, scale dissolvers may offer better corrosion control and scale inhibitor compatibility when spent, but will be higher cost. Organic acids could offer a compromise which allows most of the system requirements to be met. Hard sulfate scale is more difficult to remove because the scale has low acid solubility compared to others (Crabtee et al., 1999).

Chemical scale removal is often the first, lowest cost and use especially when scale is not easily accessible or exists where conventional mechanical removal methods are ineffective or expensive to deploy. As example, carbonate minerals are highly soluble in hydrochloric acid and therefore can be easily dissolved. HCl may be the most cost effective treatment to remove calcium carbonate, but corrosion control, system compatibility and inhibitor adsorption may all be difficult in a combined treatment.

Acetic acid (CH_3COOH) is the example of the organic acids that used to remove the scaling. It will slow down the reaction with the carbonates compared with using HCl, and they are less corrosive than HCl. The reducing acid, formic acid, and buffered blends with formate ions can be useful to reduce corrosion problems in carbonate scale removal at high temperature (Proctor, 2000; Williams et al., 2005).

According to Bezemer and Bauer (Bezemer & Bauer 1969), the most common classes of inhibitor chemicals are inorganic phosphates, organophosphorous compounds and organic polymers. Polyphosphonocarboxylic acid (PPCA) and Diethylenetriaminepenta (methylenephosphonic acid) (DETPMP) are two common commercial scale inhibitors used in the oil and gas industry. Normally, PPCA is regarded as nucleation inhibitor and DETPMP as a growth inhibitor (Chen et al., 2004).

The conventional complexing agents such as HEDTA (hydroxyethylethylenediaminetriacetic acid), EDTA (ethylenediaminetetraacetic acid), and DTPA (diethylenetriaminepentaacetic acid), and are used in washing and cleaning agents in different branches of industry, the major use being in detergent component (P.Pitter & Kora, 2001). Meanwhile, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA) and nitrilotriacetic acid (NTA) are the anthropogenic chelating agents that form stable, water soluble complexes with various metal cations. They are used in many industrial processes and consumer products among which the paper and pulp industry as well as the nuclear industry are the most important (Knepper, 2003).

The first synthesis of a compound from the group aminopolycarboxylic acids (APCAs) example of NTA (nitrilotriacetic acid) was described by Heintz in 1862 (Heintz, 1862). Much later in 1935 I.G. Farbenindustrie carried out the synthesis of EDTA (ethylenediaminetetraacetic acid) which consisted in the reaction of monochloroacetic acid with ethylenediamine in the presence of sodium hydroxide. Another way to obtain

EDTA is the reaction of ethylenediamine with sodium cyanide and formaldehyde in the presence of sodium hydroxide. Depending on the amine used also other APCAs can be obtained using this method.

The system of EDTA transport is based on its extracellular evolution with metal ions found in the solution and intracellular absorption and precipitation of metals combined with EDTA to form complexes (Witschel et al., 1999). EDTA which is conjugate base that work well on deposits that require chemical approach beside hydrochloric acid. EDTA treatment is more expensive and slower than hydrochloric acid. EDTA is effective in non-carbonate scale removal and show promise for the removal of calcium sulfate and mixture of calcium – barium sulfate.

APCAs are used as components or process chemicals in a wide variety of applications, pulp and paper, cleaning, chemical processing, agriculture and water treatment constitute 80% of their consumption. APCAs are used for:

i. Pulp and paper production
    - Stabilization of ozone and hydrogen peroxide action on pulp by complexing with metal ions (especially Fe, Cu and Mn that catalyze their decomposition), prevention from brightness reversion and protection of bleach potency.

ii. Household and industrial cleaning
    - Removal of hard water scale, soap film and inorganic scales, for example to improve the bottle cleaning in the beverage industry.
    - Detergents, soaps processing – prevention from precipitation of calcium and magnesium salts (deliming action) and their deposition on clothes, prevention soaps from becoming rancid, intensification of the adhesion of dirty surface and the cohesion of dirt particles to each other due to complexing metal ions (to better soil removal during laundering), to prevent from decomposition of bleaching agents such as sodium perborate, inhibition of color changes, stabilization of hydrogen peroxide in liquid detergents for special requirements; to enhance the antibacterial effect.

- Cosmetics industry – stabilization of creams, lotions and emulsions, reduction of allergic reactions to nickel and chromium, hair preparations, shampoos and almost every type of personal care formulation, blue color of the $[Cu(edta)]^{2-}$ complex is used in many shampoos.

iii. Water treatment

- To scale control; control water hardness and scale-forming calcium and magnesium ions.

iv. Textile industry

- To remove trace metal impurities in all phases of textile processing, particularly the scouring, dyeing and color stripping stages.

v. Metalworking

- For surface preparation, metal cleaning, metal plating and in metalworking fluids.

vi. Consumer products

- Food industry by complexing metal ions to prevent from oxidation processes leading to color changes especially in the case of canned food, for example vegetables;
- Pharmaceuticals - stabilize formulations, antioxidants and anticoagulants added to stored blood in blood banks ($[K_2(H_2edta)]$) to prevent clotting; $[NaFe(edta)]$ and $[Na_2(H_2edta)]$ added to typical iron fortification compounds in cereals increasing the adsorption of iron in adult humans, Gd(III) complex with DTPA is used as a contrast agent in diagnosis by nuclear magnetic resonance imaging.

vii. Photographic industry

- Prevention from precipitation of calcium and magnesium salts onto the photosensitive layer, $[NH_4Fe(edta)]$ complex is used as an oxidizing agent for Ag in bleach baths.